Vibrational Spectroscopy at High Pressures in CF$_4$: Implications to the Phase Diagram

H.E. Lorenzana, M.J. Lipp, W.J. Evans and N. Hemmi

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Vibrational Spectroscopy at High Pressures in CF_4: Implications to the Phase Diagram

Hector E. Lorenzana, Magnus J. Lipp, William J. Evans and Naoki Hemmi

Physics and Advanced Technologies Directorate,
Lawrence Livermore National Laboratory, Livermore, California 94551, USA

The molecular analogue of methane, CF_4 is the most fundamental saturated perfluorocarbon, exhibiting complex optical behavior that is highly unusual for such a simple molecular system. We present Raman measurements in solid CF_4 over a wide range in pressure from 1.6 to over 30 GPa at room temperature. The Raman spectra exhibit polarization-dependent intensity variations and history-dependent absence or presence of high pressure modes. Our results compellingly demonstrate that previously identified phase transitions in CF_4 based on Raman signatures need to be reconsidered. Though our data suggest possible new high-pressure transitions, we do not identify new phases because of spectral complexity. Finally, we used the measured longitudinal and transverse optical mode splitting to estimate the dipole moment derivative at high pressures and find it close to that of gaseous CF_4.

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1. INTRODUCTION

Carbon tetrafluoride, CF_4, is an analogue of methane and the most fundamental perfluorocarbon. Because of its simplicity and high symmetry, a considerable body of research exists investigating the properties of this model system.[1-13] Its commercial significance has recently been growing with the development of dry etching technology in the microelectronics industry. It is also a detonation by-product, and understanding its chemical and physical properties is crucial to modeling the physics of high-explosives. Pressure is a powerful probe of interatomic potentials, and hence, it is no surprise that a number of phase transitions in CF_4 have been identified at high pressures.[12,13] We report here Raman studies of CF_4 between 1.6 and

32 GPa. We observe remarkable richness in the measured spectra resulting from strong dependencies on laser polarization, sample orientation, and preparation history. This complexity is surprising given the fundamental simplicity of CF_4. Previous Raman studies have not reported observation of similar optical intricacies. Thus, we conclude that high-pressure transitions previously determined through changes in Raman signatures need to be revisited and potentially revised. Finally, we have determined the longitudinal and transverse optical mode (LO-TO) splitting under pressure in the ν_3 manifold of modes. Because these modes are masked by the strong diamond phonon line, we performed these measurements using sapphire anvil cells. We estimate the dipole moment derivative $\partial\mu/\partial Q$ of the high-pressure solid phases to be 219 ± 20 cm$^{3/2}$s^{-1} (phase II) and 210 ± 19 cm$^{3/2}$s^{-1} (phase III), close to the accepted value for gaseous CF_4 of 220 cm$^{3/2}$s^{-1}.[14]

2. BACKGROUND

A considerable body of work investigating the properties of CF_4 exists, including NMR[4], neutron diffraction[5], X-ray diffraction[6–8], as well as spectroscopic studies.[9–11] High-pressure studies of the properties of CF_4 exist for modest pressures below 12 GPa.[12,13]

CF_4 is a tetrahedral molecule (T_d), having four fundamental internal vibrational modes, all of which are Raman active: ν_1 (totally symmetric stretching, A_1), ν_2 (doubly degenerate bending, E), ν_3 (triply degenerate antisymmetric stretching, F_2), and ν_4 (triply degenerate bending, F_2). CF_4 freezes into the orientationally disordered or plastic phase I, at 89.5 K at atmospheric pressure. Unlike most molecular crystals with high symmetry such as methane, phase I has been reported to be non-cubic.[7] Below 76.2 K, CF_4 transforms to phase II, a well-ordered monoclinic structure of the space group C2/c (C_{2h}) with four molecules in the unit cell.[15] The liquid as well as phases I and II have been studied by Raman spectroscopy.[9,11] Fournier *et al.*[9] observed a large splitting of the triply degenerate stretching mode (ν_3) in phase II and pointed out that the splitting is associated with the longitudinal and transverse optical modes. Recently, Sasaki *et al.*[12] measured Raman spectra of CF_4 under pressures up to 8 GPa at 300 K, reporting several phase boundary traversals. Sasaki *et al.* concluded that the liquid to phase I, phase I to II and phase II to III transitions occur at 1.86, 2.84 GPa and 3.5 GPa, respectively. They also proposed a monoclinic structure (P2$_1$/c) for phase III by drawing upon similarities to CCl_4.[16,17] Nakahata *et al.*[13] recently performed X-ray powder diffraction of phase III and suggested that P2$_1$, P2$_1$/m, and P2$_1$/c groups are reasonable candidates. This latter work

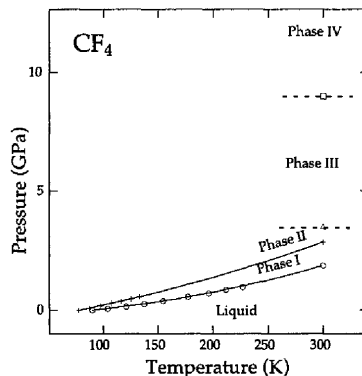**Vibrational Spectroscopy at High Pressures in CF$_4$**

Fig. 1. Phase diagram of CF$_4$ after Refs. 4–13. Dashed lines are guides to the eye.

also proposes the existence of a new phase transition at 9 GPa from phase III to phase IV based on broadening of X-ray diffraction peaks and a change of slopes in Raman frequencies as a function of pressure. These data are summarized in the phase diagram presented in Fig. 1.

3. EXPERIMENTAL TECHNIQUE

We performed a total of five separate experiments using CF$_4$ of 99.97% and 99.999% purities for the initial three and final two experiments, respectively. The highest pressures reached were about 32 GPa. The pressure variation across the sample increased with pressure up to a maximum of $\sim$2 GPa, though we minimized this effect by using appropriate spatial filtering methods. Raman spectra were collected using the 488 nm line of an argon ion laser focused to a spot size of $\sim$20 μm with typical incident power levels of 75 mW. The high pressure and optical techniques used here have been described in detail previously.[18]

4. RESULTS

Despite expectations of simplicity, the behavior under compression of CF$_4$ has turned out to be unexpectedly rich and complex. Differences between our initial experiments and previous reports led us to perform five separate experimental runs to attempt reconciliation of the data sets. Some of the differences in the spectra were found to result from crystallographic orientation and light polarization dependencies. Our samples also exhibited
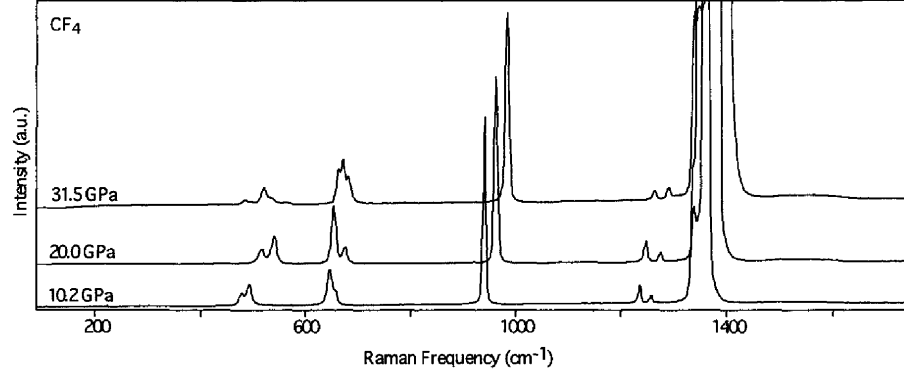
Fig. 2. Typical Raman spectra of CF_4 at various pressures. The spectrum at 31.5 GPa is from the heated sample, and the others are from run 5. Spectra are shifted vertically for clarity and normalized with respect to the ν_1 mode. The strong feature at 1300 cm^{-1} is the phonon mode of the diamond anvil.

strong history-dependent behavior. While detailed presentation of our work is beyond the scope of this report, we will draw out the important features and trends. In our effort to organize our data, we have grouped peaks into manifolds that reflect nomenclature used for the gas phase. It is important to note that we do not assume that the modes within a manifold share the same symmetry or for that matter necessarily reflect similar degrees of freedoms. For example, some modes have the potential for being overtones, combination, or isotopic bands. With this caveat, we now present the behavior of each vibrational manifold individually.

4.1. Mode ν_1

The ν_1 mode exhibited relatively simple behavior and is by far the most prominent mode in the Raman spectrum at all pressures (Figs. 2 and 3b). We observed excellent agreement with the previous data of Nakahata *et al.* However, data from Sasaki *et al.* exhibited a steeper slope and showed systematically higher peak frequencies, amounting to a difference of $\sim$8 cm^{-1} by 7.5 GPa. The pressure dependence we observed was approximately linear ($\sim$2.0 cm^{-1}/GPa). There appears to be a subtle change in slope at $\sim$16 GPa, thought the data is not statistically sufficient to bear this out. At the highest pressures, we observed some broadening of the ν_1 linewidth ranging from 3.5 to 8 cm^{-1}, likely the result of pressure gradients.

Vibrational Spectroscopy at High Pressures in CF_4
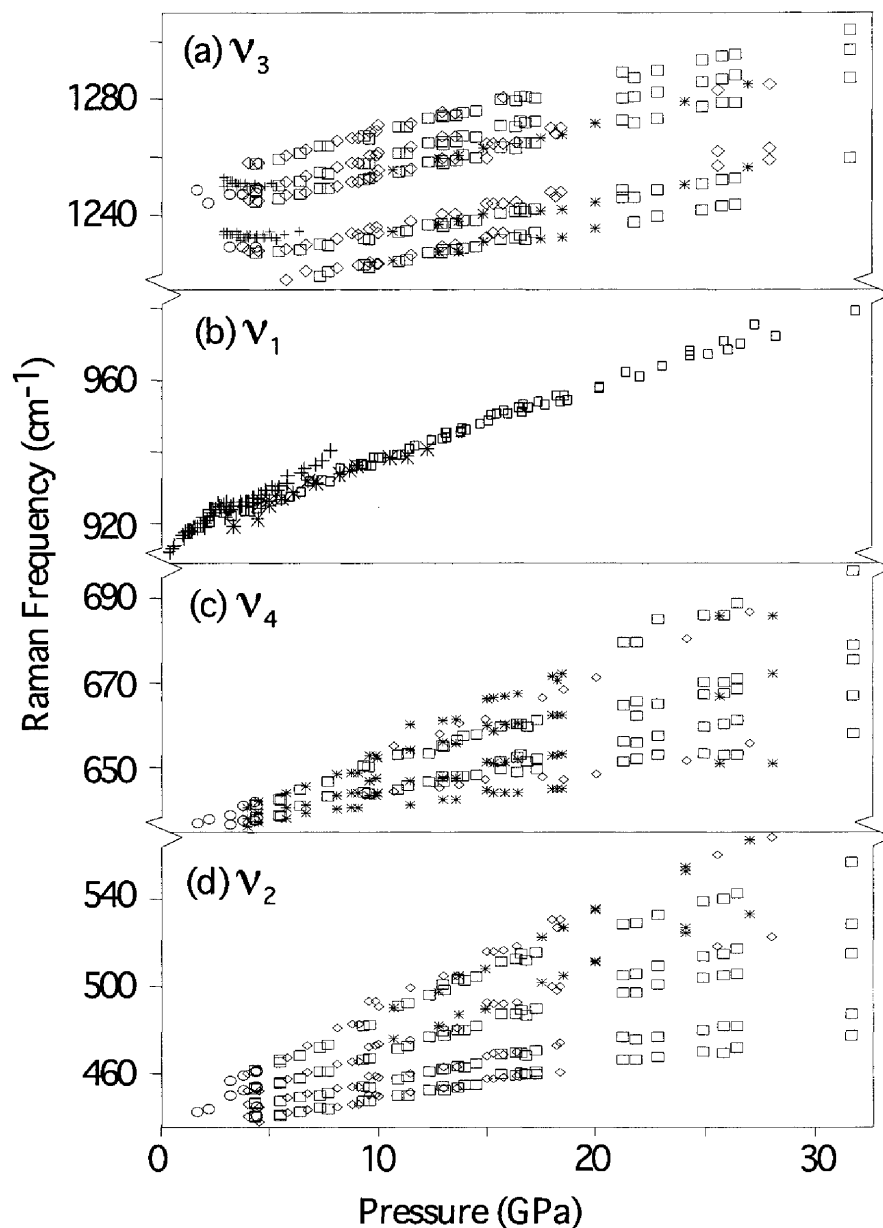
Fig. 3. Pressure dependence of the peak frequencies for the four major manifolds. For panels a,c, and d: diamonds, squares, and asterisks represent peak frequencies for experimental runs 1-3 (combined together), 4 and 5 respectively. Circles are initial data of run 4 before laser heating. Crosses are data of Ref. 12. In panel b: squares, crosses and x's represent runs 1-5 (combined together), data of Ref. 12 and data of Ref. 13 respectively.
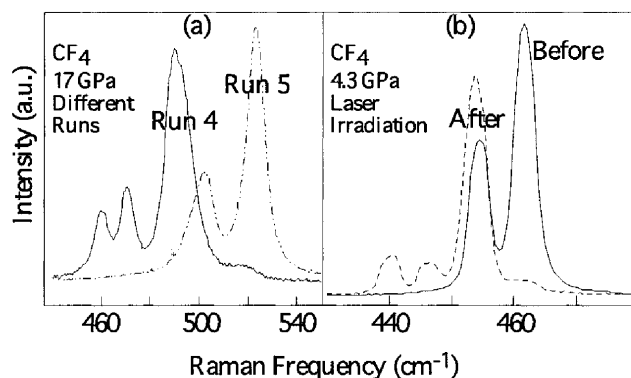
Fig. 4. Raman spectra of the ν_4 manifold showing the variation in the character of the spectra for: (a) two different runs at the same pressure and (b) a sample that was irradiated with $\sim$7 W of focused (spot 20 μm) 488 nm laser light.

4.2. Manifold ν_2

The pressure dependent behavior of the ν_2 manifold exhibits a remarkable amount of complexity as evident from Figs. 3d and 4. Comparisons between runs (Fig. 3d) show the presence or absence of several of the modes at nominally the same P-T conditions. This latter point is clearly demonstrated in Fig. 4a, where spectra from two different samples at approximately the same pressure exhibit markedly different lineshapes and number of peaks. A third sample (run 4) demonstrated the signature of phase II well into the P-T regime associated with phase III. Heating of this seemingly metastable sample at 4.3 GPa produced a dramatic change in the intensity ratio of the 4 submodes (Fig. 4b). Sasaki *et al.* and Nakahata *et al.* observe the highest frequency submode only between 2.5 and 3.5 GPa, in contrast to our observation of this mode in all of our samples and at all pressures above 3 GPa. At a pressure greater than $\sim$16 GPa one submode appears to split for the heated sample. This lends support to the possibility of a transition at $\sim$16 GPa as suggested by the slight slope change observed previously for the ν_1 mode, although the absence of a clear splitting in our other samples complicates this interpretation.

4.3. Manifold ν_4

For individual runs, the presence and absence of several of the ν_4 modes is observed, as similarly manifested in the ν_2 manifold. Although not in-

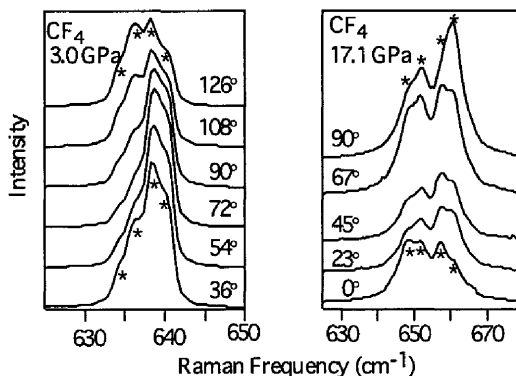**Vibrational Spectroscopy at High Pressures in CF$_4$**

Fig. 5. Representative Raman spectra of ν_4 manifold showing the polarization dependence of CF$_4$ samples at 3.0 GPa and 17.1 GPa. The angle values refer to the angular displacement between the polarizer and analyzer axes. The beam paths of the Raman excitation laser and Raman scatter collection paths are 45 degrees relative to each other. Asterisks indicate mode positions.

cluded in the Fig. 3c, we find reasonably good agreement with the data of Sasaki *et al.* and Nakahata *et al.* This mode initially appears as a doublet at 3.0 GPa. These modes shift linearly with pressure with the higher frequency submodes exhibiting somewhat larger slopes. For the heated sample (run 4) the two components show further splittings at ~16 GPa. This behavior appears to be associated with pressure dependent splittings described above for the ν_2 manifold. As with the ν_2 manifold, the unheated samples do not exhibit this splitting and the two modes' frequencies are slightly higher and lower than those of the heated sample. We also observed dramatic changes in the relative intensities of the submodes depending on the polarization of the incident Raman excitation laser. For example, Fig. 5 shows two polarization dependent Raman spectra of two of our CF$_4$ samples at 3.0 GPa and 17.1 GPa.

4.4. Manifold ν_3

The ν_3 modes are the weakest of the four branches, more than 10 times less intense than the dominant ν_1 mode. The only previously published data are those of Sasaki *et al.*, which show two excitations around 1231 and 1251 cm^{-1}. In contrast to our results, their data do not show any clear dependence on pressure up to 6 GPa (Fig. 3a). The Raman mode intensities are also sensitive to the incident laser polarization as well as P-T treatment of the

sample. The observed peak positions for different runs were of comparable frequencies, but in addition to changes in relative intensity, some excitations observed in one sample were completely absent in others. We note that the variation of the peak positions do not show significant scatter for each run individually. This suggests that observed differences are not experimental scatter but instead a manifestation of the detailed state and history of the sample. The lowest frequency peak is weak and likely results from isotopic impurities (^{13}C).[11]

5.   DISCUSSION

5.1.   Crystal Structure and Spectral Character

The complexity of the high pressure spectral characteristics of CF_4 is indicative of a low symmetry crystal structure. The crystal structure of CF_4 in phase II has been suggested to be monoclinic and the same has been suggested for phase III. Based on the increasing complexity of the Raman spectra, it is clear that only low symmetry structures are consistent with our data up to pressures of 32 GPa, though the actual structure may elude us at the present. For example, group theoretical analysis of the $P2_1/c$ structure suggested by Sasaki *et al.* permits 12 modes,[19,20] and we experimentally observe up to 12 modes until ~10 GPa, where the number of modes increases, reaching 15 at the highest pressures.* We conclude that structural predictions based on group theoretical arguments must at least account for all of the observed Raman modes. As has been amply demonstrated by our measurements, the presence of the modes depends on the P-T history of the sample. Thus even our measurements can only be considered to be a lower bound on the number of Raman active modes in this system.

The orientation of crystallites with respect to the incoming laser light may be the source of the rather complex behavior observed in the Raman spectra of high pressure CF_4 and the variation among different runs including those reported in the literature. For example, one key difference between our experiments and Sasaki *et al.* is that they strove to grow a single crystal of CF_4 from the liquid whereas we did not. However, we place an important caveat here. We were never able to extinguish a peak nor able to observe a peak that was completely absent by varying only the polarization optics. Thus the very plausible possibility exists that preparation conditions may actually affect not only crystallographic orientation and microstructure but

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*We have preliminary observations of extremely weak peaks in the 100 cm^{-1} regime consistent with librational and other lattice modes. Further measurements need to be performed to understand the modes' reproducibility, nature and crystallographic information.

also the final phases.

Interpretation of our polarization measurements would benefit from knowledge of the crystallographic orientation of the high-pressure CF_4 crystallites. Our samples were captured in the liquid phase and pressurized into the solid phase. It is well-known that preferred crystalline orientation[21] as well as stabilization of different phases dependent on P-T history[22] have been oberved in diamond anvil samples loaded in this fashion. X-ray scattering measurements could resolve this issue by measuring the crystal structure and correlating measurements of orientation to the associated Raman spectrum.

5.2.   Laser Heating and Metastability

The laser heating of the sample raises several interesting issues. It is clear that the laser heating altered the sample, but the nature of the change is not obvious. The laser potentially annealed the sample and in so doing reoriented the crystalline axes. This result would be consistent with the appearance of new Raman modes that were previously absent. Alternatively, the heating may have transformed the sample to a new phase that then persisted metastably. As mentioned above, x-ray scattering measurements can resolve this question conclusively.

In the course of these experiments, we have observed mild hysteresis in several of the samples. Specifically upon decompression, spectral signatures of phases II and III could persist metastably $\sim$0.5 GPa below their expected transition pressures. Similarly, the spectral character of phase II was metastably preserved to $\sim$1 GPa above its expected transition pressure. These examples of hysteresis suggest that the absence of some of the Raman lines at higher pressures might be a metastability issue.

5.3.   Phase Transitions above 5 GPa

Our data do not lend strong support to any transition above phase III. With regard to the phase transition III to IV proposed by Nakahata *et al.* at $\sim$9 GPa, our data do not show any accompanying change in the Raman spectra. There is a possible phase transition at $\sim$16 GPa, as weakly suggested by the ν_2 and ν_4 manifolds. Because of the complexity in the Raman data, however, we conclude that the data are currently not adequate to support identification of new phases.
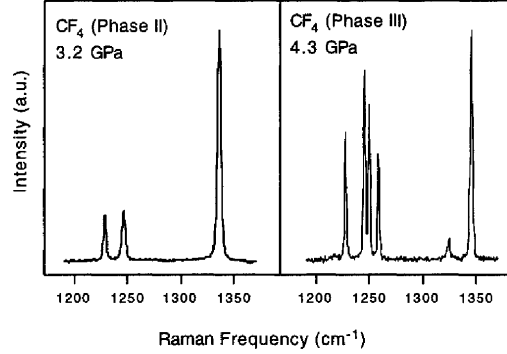
Fig. 6. Raman spectra taken using sapphire anvil cells showing the full ν_3 manifold of CF_4 samples at 3.2 GPa and 4.3 GPa. Normally with the use of a diamond anvil cell, the spectra around 1300 cm^{-1} would be masked by the intense diamond phonon line.

5.4. LO-TO splitting

Raman spectra using sapphire anvils were collected in phase II and phase III (Fig. 6). In both phase II and phase III, the ν_3 manifold exhibits large splittings between two distinct groups of submodes. Given such a large frequency difference, it is unlikely that the these two groups result from only crystal field effects. As investigated in the low temperature crystalline phase studies of CF_4[9,11] and SiF_4,[23] the behavior of ν_3 is well-explained by the assumption that a splitting into longitudinal and transverse optical modes (LO and TO modes) arises from dipole-dipole interactions. Since one of these groups of lines is masked by the intense 1330 cm^{-1} diamond phonon line, sapphire anvil cells were necessary for these experiments. The presence of LO-TO splitting due to dipole transition interactions has been observed in many ionic crystals, but rarely in molecular solids. CF_4 is one of the few molecular solids that exhibit LO-TO splitting in low-temperature solid phases.[23,24] For cubic systems, the frequencies are related to the dipole derivative $\partial\mu/\partial Q$ by,[14,25]

$$\frac{\partial\mu}{\partial Q} = \pm\left(\frac{3}{n_0^2+2}\right)\sqrt{\left[\frac{\pi n_0^2\left(\nu_{LO}^2-\nu_{TO}^2\right)}{N}\right]} \tag{1}$$

where ν_{LO} and ν_{TO} are respectively the longitudinal and transverse frequencies, n_0 is the refractive index on the high frequency side of the band, and N is the number of oscillators per unit volume. Although derived for cubic systems, this relation has been applied more generally to other structures, including liquid phases with reasonable results.[11] The dipole derivative was

calculated for the ν_3 multiplets in phase II and III. For comparison we have also performed this calculation for the data of Gilbert *et al.* in phase II (P=1 atm, T=77 K). Since the LO and TO modes split into multiplets, we averaged the frequencies of these multiplets to arrive at a representative value for each group of modes. The only reported density measurement of high-pressure CF_4 is the data of Nakahata *et al.* at 7.5 GPa. They measured a density of 29.48 cc/mol at 7.5 GPa and 300 K (phase III),[13] as compared to 42.7 cc/mol at 1 atm and 74 K (phase II).[7] As stated our measurements for phase II and III are at 3.2 and 4.3 GPa respectively, close to the middle of the range of these two data points. Given this scarcity of data, we report the average of the calculated dipole derivative at these two density extremes with an uncertainty encompassing the range of these limiting values. The above relation is very weakly sensitive to the index, so we set n_0 at the value of 1.4 suggested by Besse *et al.*[23] Using these assumptions and model, we calculate values of 219 ± 20 and 210 ± 19 $cm^{3/2}s^{-1}$ for high pressure phases II (3.2 GPa) and III (4.3 GPa). These values are close to the CF_4 gas phase value of 220 $cm^{3/2}s^{-1}$ measured by Schatz *et al.*[14] and also the value of 220.2 $cm^{3/2}s^{-1}$ which we calculate for phase II at 70 K and 1 atm using the data of Gilbert *et al.* That such a simple model yields reasonable values for this important electronic parameter is remarkable and perhaps fortuitous.

6. CONCLUSIONS

High-pressure solid phases of CF_4 have been studied up to 32 GPa at room temperature by Raman scattering. A rich complexity in the Raman spectra, characteristic of a low symmetry structure was observed to the highest pressures of this study. Our Raman spectra showed no clear evidence of a transition at 9 GPa as previously reported. There are indications that a transition may be ensuing around 16 GPa, but because of the complexity of the behavior in our samples, corroborating measurements need to be performed. Using a simple model, the derivative of the dipole moment, $\partial\mu/\partial Q$, in the high-pressure solid phase was determined to be 219 ± 20 and 210 ± 19 $cm^{3/2}s^{-1}$ for phases II and III. The intricate character of this system at high pressures is very surprising given the simplicity of the CF_4 molecule and warrants further study with an emphasis on x-ray structural measurements.

ACKNOWLEDGMENTS

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REFERENCES

1. K. Maki, Y. Kataoka, and T. Yamamoto, *J. Chem. Phys.* **70**, 2688 (1979).
2. T. Shinoda, *Mol. Cryst. Liq. Cryst.* **55**, 101 (1979).
3. R. Savoie in *The Raman Effect, Vol. 2*, ed. by A. Anderson, Marcel Dekker, New York (1973), p.759.
4. D. Putten, K. Prins, P. Kortbeek, and N. Trappeniers, *J. Phys. C* **20**, 3161 (1987).
5. I. Waldner, A. Bassen, H. Bertagnolli, K. Todheide, G. Strauss, and A. Soper, *J. Chem. Phys.* **107**, 10667 (1997) .
6. R. Harris and G. Clayton, *J. Chem. Phys.* **45**, 2681 (1966).
7. S. Greer and L. Meyer, *J. Chem. Phys.* **51**, 4583 (1969).
8. D. Bolshutkin, V. Gasan, A. Prokhvatilov, and A. Erenburg, *Acta. Cryst. B* **28**, 3542 (1972) .
9. R. Fournier, R. Savoie, F. Bessette, and A. Cabana, *J. Chem. Phys.* **49**, 1159 (1968).
10. Y. Sataty, A. Ron, and F. Herbstein, *J. Chem. Phys.* **62**, 1094 (1975).
11. M. Gilbert and M. Drifford, *J. Chem. Phys.* **66**, 3205 (1977).
12. S. Sasaki, Y. Ikeda, and H. Shimizu, *J. Phys. Soc. Japan* **60**, 1560 (1991).
13. I. Nakahata, N. Matsui, Y. Akahama, M. Kobayashi, and H. Kawamura, *Rev. High Pressure Sci. Tech.* **7**, 802 (1998).
14. P. Schatz and D. Hornig, *J. Chem. Phys.* **21**, 1516 (1953).
15. G. Pepe and J. Gay, *J. Chem. Phys.* **90**, 5735 (1989).
16. G. Piermarini and A. Braun, *J. Chem. Phys.* **58**, 1974 (1973).
17. A. Anderson, H. Basista, B. Torrie, and W. Zeng, *Chem. Phys. Lett.* **117**, 240 (1985).
18. H. E. Lorenzana, J. E. Klepeis, M. J. Lipp, W. J. Evans, H. B. Radousky, M. van Schilgaarde, *Phys. Rev. B* **56**, 543(1997).
19. A. Anderson, B. H. Torrie and W. S. Tse, *Chem. Phys. Lett.* **61**, 119 (1979).
20. D. M. Adams and S. K. Sharma, *J. Chem. Soc. Dalton Trans.*, 2424 (1976).
21. P. Loubyere, R. LeToullec, D. Hausermann, M. Hanfland, R. J. Hemley, H. K. Mao and L. W. Finger, *Nature* **383**, 702 (1996).
22. R. L. Mills, J. L. Yarnell, and A. F. Schuch in *Low Temperature Physics-LT 13, Vol. 2*, ed. by K. D. Timmerhaus, W. J. O'Sullivan and E. F. Hammel, Plenum Press, New York (1974), p. 616.
23. F. Bessette, A. Cabana, R. Fournier, and R. Savoie, *J. Chem. Phys.* **48**, 410 (1970).
24. M. Pezolet and R. Savoie, *Can. J. Spectry.* **17**, 39 (1972).
25. C. Haas and D. Hornig, *J. Chem. Phys.* **26**, 707 (1957).